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(54) Title: POLYESTER COMPOSITION HAVING IMPROVED GAS BARRIER PROPERTIES

(57) Abstract

Polyester compositions are disclosed for use in the form of a film or container having improved gas barrier properties comprising homo– or copolyesters derived from terephthalic acid or mixtures of terephthalic acid with 2,6–naphthalene dicarboxylic acid or isophthalic acid and a glycol component, such as ethylene glycol, and containing from 5 to 17 mole % of a biphenol aromatic hydroxy compound. Films of these compositions are characterized by having greatly reduced oxygen permeabilities and can be used for packaging materials, particularly, for packaging food or drink.

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TITLE
POLYESTER COMPOSITION HAVING IMPROVED GAS BARRIER PROPERTIES

BACKGROUND OF THE INVENTION

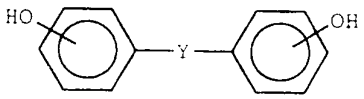
This invention relates to a polyester composition, and in particular to an article, such as a film or container produced therefrom having improved gas barrier properties.

Polyester materials are particularly suitable for forming into films, containers and bottles for use as packaging materials for foodstuffs and beverages such as soft drinks and beer. Unfortunately, polyester materials are permeable to some extent to gases such as carbon dioxide, and the ingress of oxygen which may affect the flavor of the packaged contents. The situation can be improved by coating the polyester film, container or bottle with a layer of barrier material which has low gas permeability, e.g., a polyvinylidine chloride copolymer. However, coated materials have various disadvantages such as the need for a relatively thick coating layer, the extra costs involved with the use of additional polymers and processing steps, toxicity and delamination.

Another approach for improving gas barrier properties involves the preparation of multilayered articles, such as bottles, containing individual barrier layers. However, this approach adds extra cost since additional layers must be used.

The present invention provides a polyester composition which can be made into an article such as a film, container or bottle which has improved gas barrier properties without the necessity of using additional coating materials or multilayer structures.

U.S. 4,474,918 discloses improvement of gas barrier properties by melting and blending a polyester with a naphthalene diol or a bisphenol of the formula



where Y is $-(CH_3)_2-$, $-SO_2-$ or -S-. When the product is actually molded into a film, gas barrier performance is improved but there is a marked reduction in mechanical properties. In the polyester composition of the present invention, Y is a direct bond and not a divalent bridging group.

Japanese laid-open patent application 4(1992)-11651 discloses a polyester composition having good gas barrier properties, transparency and mechanical properties obtained by adding from 0.1 to 30 parts by weight of 1-naphthol,

2-naphthol, triphenylcarbinol, hydroquinone, resorcinol or catechol to 100 parts by weight of the polyester.

The polyester composition of the present invention differs from the aforementioned prior art polyester compositions in that it contains a specific 4,4'-biphenol, 2,2'-biphenol or 3,3'-biphenol aromatic hydroxy compound or mixed biphenol isomers or mixtures thereof, which provides greatly improved gas barrier properties without the loss of transparency or reduction in mechanical properties.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a polyester composition having improved gas barrier properties comprising a dicarboxylic acid component selected from the group consisting of terephthalic acid and mixtures of terephthalic acid with up to 5 mole % of 2,5-, 2,6- or 2,7-naphthalene dicarboxylic acid or isophthalic acid and an aliphatic glycol component containing from 2 to 16 carbon atoms, wherein the polyester composition contains from 1 to 17 mole %, based on the total molar amount of the polyester, of an aromatic hydroxy compound selected from the group consisting of 4,4'-biphenol, 2,2'-biphenol, 3,3'-biphenol, biphenol mixed isomers and mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

The polyester component of the present invention may be a synthetic thermoplastic polyester, particularly a synthetic linear polyester, obtained by condensing terephthalic acid or its lower alkyl (up to 6 carbon atoms) diester with one or more aliphatic glycols containing from 2 to 6 carbon atoms. Mixtures of terephthalic acid or ester containing up to 5 mole % of 2,5-, 2,6- or 2,7-naphthalene dicarboxylic acid or isophthalic acid may also be used.

Aliphatic glycols include ethylene glycol, propylene glycol, diethylene glycol, 1,2-propylene glycol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2,4-trimethyl-1,3-pentanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. Particularly preferred is ethylene glycol which when used herein may also contain diethylene glycol in amounts of from 0.5 to 2.5 mole % based on the total moles of ethylene glycol present.

Polyethylene terephthalate (which term herein includes not only the homopolymer formed by poly-condensation of hydroxyethyl terephthalate but also copolymers containing up to 5 mole % of units derived from naphthalene

dicarboxylic acid or isophthalic acid and other aliphatic glycols) is particularly preferred.

The inherent viscosities (IV) of the polyesters herein are determined according to ASTM Method D2857 using a Cannon Ubbelhohde viscometer using a polymer concentration of 0.5% by weight in 25/75 by volume trifluoroacetic acid/methylene chloride at 30 ± 0.1°C. The IV of the polyester composition of the invention can range from 0.50 to 0.60 dl/g or higher. If the IV is less than 0.50, an undesirable reduction in mechanical properties may occur.

According to the present invention, gas barrier properties of a polyethylene terephthalate composition surprisingly can be greatly improved by incorporating from 1 to 17 mole %, preferably from 5 to 12 mole %, based on the total molar amount of the polyester, of an aromatic hydroxy compound selected from 4,4'-biphenol, 2,2'-biphenol, 3,3'-biphenol, mixed biphenol position isomers including 2,3'-biphenol, 3,4'-biphenol and 2,4'-biphenol resulting from the oxidative coupling of phenol and mixtures thereof. A biaxially stretched, heat-set film formed from the polyester composition has an oxygen permeability of less than 3.0 cc-mil/100 in^2-24 hours-atm. The PET composition also exhibits excellent transparency and mechanical properties.

If the content of the aromatic hydroxy compound is less than 1 mole %, the improvement in the gas barrier properties of the polyethylene terephthalate composition may be insufficient for some applications. On the other hand, if the content of the aromatic hydroxy compound exceeds 17 mole % the polymer melting point and crystalline character decrease dramatically, thereby adversely affecting the transparency and mechanical properties.

In another embodiment of the invention, the gas barrier properties of a polyethylene terephthalate composition can be improved by using 4,4'-biphenol, 2,2'-biphenol, 3,3'-biphenol, biphenol mixed isomers or mixtures thereof in the form of an oligoester comprising the biphenol compound, the dicarboxylic acid component and the glycol component having a number average molecular weight of less than 4000.

The dramatic improvement in gas barrier properties obtained in the present invention is believed partly due to the presence of biphenol units introduced into the PET which can provide unique crystallization sites as well as chain stiffening segments and reduce free volume, thereby uniquely hindering the diffusion of gas while improving mechanical properties. In addition, high gas barrier can arise from the reduction in localized motion along the molecular backbone, i.e., hindrance to micro Brownian motion, due to interaction of phenolic chain ends on the polymer molecules and free biphenol with polyester molecules.

The polyester compositions are prepared by blending the aromatic hydroxy compound with the PET, and melting and kneading the blend in an extruder to form mixed chips or pellets. Copolyester compositions of the invention may also be formed by direct polymerization of the aromatic hydroxy compound and PET monomer components.

If desired, conventional additives such as dyes, pigments, stabilizers, plasticizers, fillers, ultraviolet absorbers, fluorescent brighteners, antistatic agents, mold release agents, and the like, may be added to the polyester composition in typical amounts.

The polyester composition of the present invention can be formed into an article such as a film, container, bottle or any similar receptacle that can be used for packaging materials, and particularly for packaging food and drink.

As regards to films, a polyethylene terephthalate film is particularly preferred, especially a film which has been biaxially oriented by sequential stretching or simultaneous stretching in two mutually perpendicular directions, typically at a temperature in the range of 70° to 125°C, preferably from 75° to 95°C, and preferably heat set, typically at a temperature in the range of 150° to 250°C, preferably from 180° to 220°C.

A polyester film prepared from a polyester composition of the invention may be unoriented, or uniaxially oriented, but is preferably biaxially oriented by stretching sequentially or simultaneously in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties. Stretching may be effected in a tenter frame by extruding the polyester as a flat extrudate that is subsequently stretched first in one direction and then in the other mutually perpendicular direction or simultaneously in both directions. Generally, it is preferred to stretch first in the longitudinal direction, and then in the transverse direction. The stretched polyester film may be, and preferably is, dimensionally stabilized by heat-setting under dimensional restraint at a temperature above the glass transition temperature thereof.

Polyester compositions of the present invention can also be fabricated into containers, such as bottles, by an injection or blow molding process wherein a preform is heated and stretched both axially and radially so as to confer biaxial orientation. The polyester hollow molded product has a high mechanical strength as well as excellent transparency and gas barrier properties, and can be widely used for fresh beverage, flavoring material, oil, alcoholic drink such as beer and wine and cosmetics. Particularly, the hollow polyester molded product can be used as a small-sized container for carbonated drink, beer, wine, or the like, which

would not be preserved for a predetermined guaranteed period due to the insufficient gas barrier property using a conventional biaxially stretched polyethylene terephthalate bottle.

The invention will be further illustrated by the following examples although it is understood that these examples are included merely for purposes of understanding and are not intended to limit the scope of the invention.

In the following examples, oxygen permeability is calculated in cubic centimeters of O_2 permeating a 1-mil thick sample, per 100 inches square, over a 24-hour period under an O_2 partial pressure difference of one atmosphere at 30°C using a Mocon OX-TRAN twin instrument and is reported as cc-mil/100 in^2-24 hours-atm.

EXAMPLES 1 TO 6
(COMPARATIVE EXAMPLES 1C TO 5C)

Polyethylene terephthalate (PET) having an IV of 0.85 dl/g was melt blended with the aromatic hydroxy compounds shown in Table I in a twin screw extruder at a temperature range of 250° to 265°C to form pellets which were dried at 120°C. Amorphous cast films having a thickness of from 5 to 10 mils were made from the dried pellets in a press heated at 270°C. The films were simultaneously stretched in the temperature range of 80° to 95°C at a stretch ratio of 3.5 X 3.5 (MD/TD) and strain rate of 9000% per minute. The films were subsequently heat-set at 180°C. Oxygen permeability values are shown in Table I. From the results, it can be seen that more than a 50% reduction in oxygen permeability (2X the barrier) was obtained for PET made by adding either 11 mole % of 4,4'-biphenol or 10 mole % of a combination of 5 mole % 4,4'-biphenol and 5 mole % of naphthalene dicarboxylic acid.

Table I

Example No.	Polyester Composition (mole %)	Stretch Ratio (MDXTD)	T_S (°C)	HST (°C)	Oxygen* Permeability	MP (°C)	IV (dl/g)
-	PET	3.5 X 3.5	85	180	6.5	255	0.85
-	PET	3.5 X 3.5	95	NHS	8.0	255	0.85
-	PET	Cast	-	-	9.9	255	0.59
1	PET-5% BP	3.5 X 3.5	80	180	3.0	250	0.52
2	PET-5% BP	3.5 X 3.5	90	180	3.0	250	0.52
3	PET-11% BP	3.5 X 3.5	85	180	2.3	245	0.55
4	PET-11% BP	3.5 X 3.5	85	NHS	2.0	245	0.55
5	PET-5% BP-5% NDCA	3.5 X 3.5	95	180	2.8	243	0.60
6	PET-5% BP-5% NDCA	3.5 X 3.5	85	180	2.7	243	0.60
1C	PET-5% BISP-A	3.5 X 3.5	90	NHS	4.3	249	0.53
2C	PET-5% BISP-A-5% NDCA	3.5 X 3.5	95	180	4.6	249	0.54
3C	PET-5% BISP-A-5% NDCA	3.5 X 3.5	80	NHS	5.1	249	0.54
4C	PET-5% BISP-A-5% NDCA	3.5 X 3.5	80	180	3.64	249	0.54
5C	PET-6% NDCA	3.5 X 3.5	95	180	4.1	-	0.60

BP = 4,4'-biphenol; BISP-A = bisphenol-A;

NDCA = naphthalene dicarboxylic acid

T_S = Stretch temperature; IV = intrinsic viscosity

NHS = not heat-set

HST = heat-setting temperature; MP = melting point

* cc-mil/100 in^2-24 hours-atm

EXAMPLES 7 TO 9
(COMPARATIVE EXAMPLE 6C)

Amorphous cast films of polyethylene terephthalate (PET) containing 3 mole % of isophthalic acid and 4,4'-biphenol were prepared as described in Examples 1 to 6. The films were stretched at a stretch ratio of 3.5 X 3.5 (MD/TD) at a stretching temperature of 85°C with strain rate of 9000% per minute. Non heat-set films were used for oxygen permeability measurements.

The results in Table II illustrate the large reduction in oxygen permeability that can be obtained using the polyester composition of the invention.

The total amount (mole %) of BP contained in the polyester film composition was determined by ^{1}H-NMR. From 4 to 7 mole % of BP provided optimum oxygen barrier properties of 50 to 66% without affecting transparency or mechanical properties.

TABLE II

Example No.	Polyester Composition (mole %)	Stretch Ratio (MDXTD)	Ts (°C)	HST (°C)	Oxygen* Permeability	MP (°C)	IV (dl/g)	% BP (by NMR)
7	PET-8% BP-3% ISP	3.5 X 3.5	85	-	2.1	241	0.50	6.5
8	PET-10% BP-3% ISP	3.5 X 3.5	85	-	2.0	238	0.49	7.0
9	PET-5% BP-3% ISP	3.5 X 3.5	85	-	2.8	244	0.57	4.2
6C	PET-3% ISP	3.5 X 3.5	85	-	5.9	246	0.72	-

ISP = isophthalate

* cc-mil/100 in^2-24 hours-atm

What is claimed is:

1. A polyester composition having improved gas barrier properties comprising a dicarboxylic acid component selected from the group consisting of terephthalic acid and mixtures of terephthalic acid with up to 5 mole % of 2,5-, 2,6- or 2,7-naphthalene dicarboxylic acid or isophthalic acid and an aliphatic glycol component containing from 2 to 16 carbon atoms, wherein the polyester composition contains from 1 to 17 mole %, based on the total molar amount of the polyester, of an aromatic hydroxy compound selected from the group consisting of 4,4'-biphenol, 2,2'-biphenol, 3,3'-biphenol, biphenol mixed isomers and mixtures thereof.

2. The polyester composition of Claim 1 wherein the glycol component comprises ethylene glycol and the aromatic hydroxy compound comprises 4,4'-biphenol.

3. The polyester composition of Claim 2 wherein the dicarboxylic acid component comprises terephthalic acid.

4. The polyester composition of Claim 2 wherein the dicarboxylic acid component comprises a mixture of terephthalic acid and up to 5 mole % of 2,6-naphthalene dicarboxylic acid.

5. The polyester composition of Claim 2 wherein the dicarboxylic acid component comprises a mixture of terephthalic acid and up to 5 mole % of isophthalic acid.

6. The polyester composition of Claim 1 wherein the biphenol mixed isomers include 2,3'-biphenol, 3,4'-biphenol and 2,4'-biphenol resulting from the oxidative coupling of phenol.

7. The polyester composition of Claim 1 wherein the polyester comprises polyethylene terephthalate.

8. An article formed from the polyester composition of Claim 1.

9. The article of Claim 8 in the form of a film having an oxygen permeability of less than 3.0 cc-mil/100 in^2-24 hours-atm.

10. The film of Claim 9 which is biaxially oriented.

11. The article of Claim 8 in the form of a bottle.

12. The bottle of Claim 11 which is biaxially oriented and formed from a preform which is stretched axially and radially.

13. The polyester composition of Claim 1 comprising an oligoester of the 4,4'-biphenol, 2,2'-biphenol, 3,3'-biphenol, biphenol mixed isomers or mixtures thereof, the dicarboxylic acid component and the aliphatic glycol component, the oligoester having a number average molecular weight of less than 4000.

14. The polyester composition of Claim 13 wherein the oligoester comprises terephthalic acid, ethylene glycol and 4,4'-biphenol.

INTERNATIONAL SEARCH REPORT

rnational Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/13 C08L67/02 C08G63/91 C08G63/193 C08J5/18
B65D1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C

[X] Patent family members are listed in annex

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